

DEPARTMENT OF THE ENVIRONMENT
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PACIFIC & YUKON REGION

THE PERSISTENCE OF TRICLOPYR AND
ITS PYRIDINOL METABOLITE IN A
COASTAL BRITISH COLUMBIA STREAM

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By

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ABSTRACT

In 1984, a monitoring study was conducted by Environmental Protection, Pacific and Yukon Region, of Environment Canada, to determine the persistence of triclopyr and its pyridinol transformation product in stream water and sediment.

Triclopyr residues in stream water reached a level of 0.620 mg/L within 0.5 hours following an aerial overspray application of Garlon 4TM at 0.91 kilograms of active ingredient per hectare (kg a.i./ha). Although triclopyr residues declined rapidly to 0.006 mg/L within 1 day, low concentrations (0.001 to 0.003 mg/L) of this herbicide were detected for two months following the spray. The pyridinol degradation product was detected in stream water 2 days post-spray at 0.070 mg/L, and thereafter at 0.030 to 0.060 mg/L for 2 months following the spray application.

Both triclopyr and its pyridinol transformation product appeared in the stream sediment at 0.14 mg/kg and 0.20 mg/kg respectively 4 hours post spray. Triclopyr and the pyridinol degradation product were also detected at low concentrations (0.02 mg/kg to 0.12 mg/kg) in sediment for four months after the spray. After this period, residues of these chemicals were not detected above the limit of detection (0.02 mg/kg) in the sediment.

RÉSUMÉ

En 1984, le Service de la protection de l'environnement, région du Pacifique et du Yukon, Environnement Canada, a procédé à une étude destinée à déterminer la persistance, dans l'eau des cours d'eau et dans leurs sédiments, du triclopyr et de sa transformation en pyridinol.

Les résidus de triclopyr trouvés dans l'eau ont atteint un taux de concentration de 0,620 mg/l dans la demi-heure qui a suivi une pulvérisation aérienne de Garlon 4TM à raison de 0,91 kg de matière active par hectare. Bien que le taux de concentration des résidus de triclopyr soit rapidement tombé à 0,006 mg/l, après la première journée, on a détecté des taux de 0,001 à 0,003 mg/l de cet herbicide pendant les deux mois qui ont suivi la pulvérisation. Quant au pyridinol, produit de dégradation du triclopyr, on en a détecté dans l'eau du cours d'eau à un taux de 0,070 mg/l 2 jours après la pulvérisation, puis à des taux de 0,030 à 0,060 mg/l au cours des 2 mois qui ont suivi cette même pulvérisation.

Le triclopyr et le pyridinol, son produit de dégradation, ont été détectés dans les sédiments du cours d'eau, aux taux de concentration respectifs de 0,14 mg/l et de 0,20 mg/l, 4 heures après la pulvérisation. Dans les 4 mois qui ont suivi celle-ci, le triclopyr et le pyridinol ont été détectés dans les sédiments à des taux de concentration faibles (de 0,02 mg/kg à 0,12 mg/kg). Après cette période, le taux de concentration des résidus de ces corps chimiques n'a pas dépassé le taux limite de détection dans les sédiments (0,02 mg/kg).

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CONCLUSIONS

1. Triclopyr and its pyridinol metabolite can be detected in very low concentrations (0.001 - 0.006 mg/L) in flowing stream water for at least two months after a direct aerial overspray.
2. These chemicals do not persist for more than 4 months in stream sediment at levels greater than 0.02 mg/kg under similar treatment conditions.
3. The degradation of triclopyr and its pyridinol metabolite in stream water and sediment is presently not well understood. Studies are required to identify the degradation processes of these chemicals.
4. The various residues of triclopyr, (i.e., triclopyr butoxyethyl ester, triclopyr acid, and the metabolite 3,5,6-trichloro-2-pyridinol) in stream water and sediment should be individually quantified in future studies.

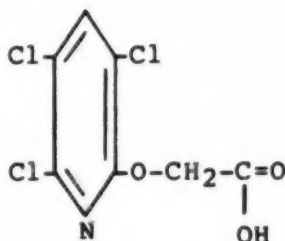
1 INTRODUCTION

Triclopyr (Garlon 4TM) is a selective post-emergent herbicide used for the control of unwanted broadleaf vegetation in agriculture and woody plants in forestry. In the coastal forest areas of British Columbia, it has the potential to replace the phenoxy herbicides 2,4-D and 2,4,5-T for conifer release programs. However, Garlon 4TM is presently not registered for forestry use in Canada.

Most of the data on environmental fate submitted for the registration evaluation of this herbicide in Canada was produced in the U.S.A., where conditions are generally warmer and dryer than in Western Canada, particularly British Columbia. Concerns were raised about the inadequate data base on the fate and persistence of this chemical in the aquatic environment. To assist the regional office of Environmental Protection in the evaluation of the potential impact of triclopyr on salmonids, a study was conducted in 1984 to determine the persistence of this herbicide and its metabolites in a coastal British Columbia stream.

2 LITERATURE REVIEW

Triclopyr is the common name for 3,5,6-trichloro-2-pyridinyloxyacetic acid represented by the following formula:



The butoxyethyl ester (BEE) of triclopyr, with a synonym of triclopyr ethyleneglycolbuthylether ester (EGBE), is formulated as an oil soluble, water emulsifiable concentrate and sold under the trade name Garlon 4TM. The proportion of triclopyr BEE to the inert ingredient in Garlon 4TM is approximately in a ratio of 2:1 (v/v). The acid equivalent of triclopyr is 44.3 % as stated on the proposed label.

Presently, there is insufficient information on the persistence and fate of triclopyr (Garlon 4TM) in the aquatic environment. According to an affidavit by J. McCall (1985), the degradation of triclopyr BEE in water involves both chemical degradation by hydrolysis and physico-chemical photolysis. The relative importance of these two processes

depends on the prevailing conditions of the aquatic environment with respect to pH, temperature, light intensity and microbial degradation.

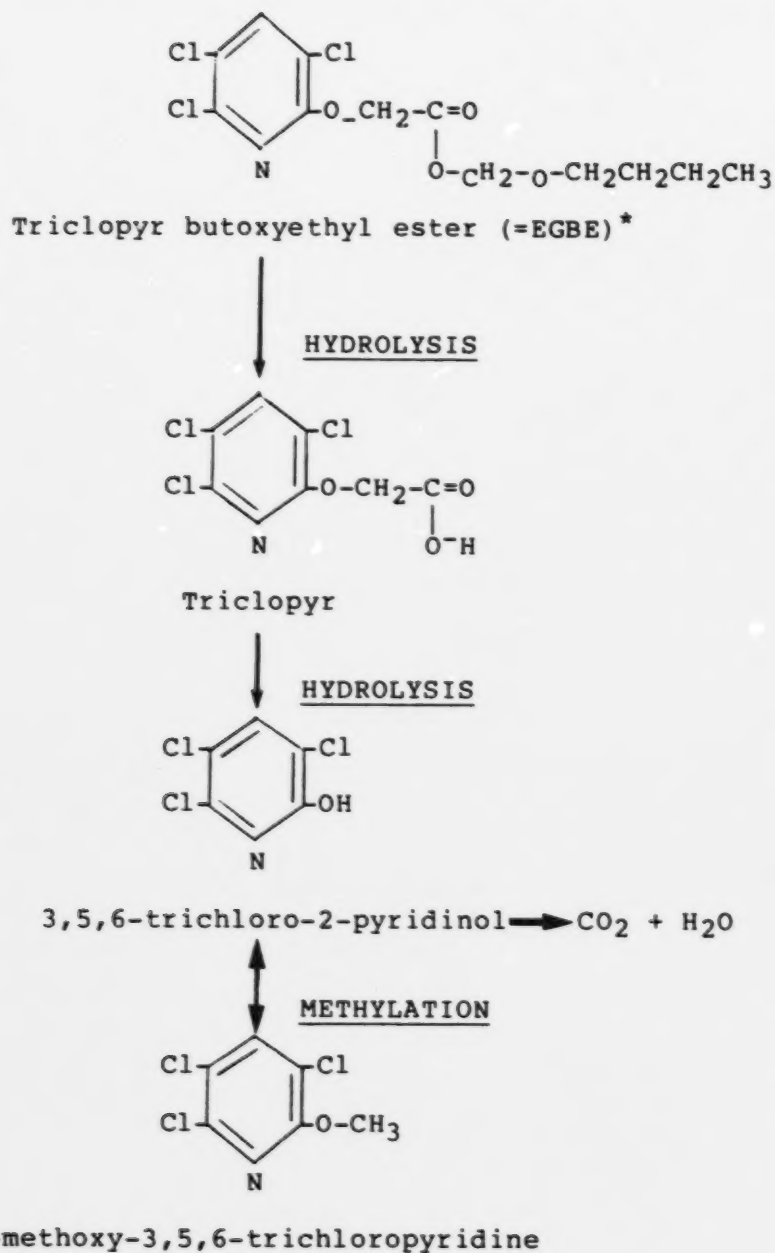
In a recent study by Bidlack and Hamaker on the fate of triclopyr butoxyethyl ester in water (as discussed in the 1985 affidavit of P.J. McCall), the first step in Garlon 4TM degradation is the hydrolysis of the ester to the triclopyr acid. The acid molecules are hydrolysed to the trichloropyridinol and then methylated to produce a trichloropyridine (Figure 1). The rate of hydrolysis is a function of pH and temperature. Triclopyr BEE hydrolyzes faster in buffered warm water (25°C) with a pH greater than 7. The half-life under these conditions is about 8 days. Under natural water conditions (unspecified pH and temperature), however, the half life is approximately one day (McCall 1985). The final degradation products of trichloropyridinol and methoxytrichloropyridine are carbon dioxide and water.

Triclopyr BEE is also degraded by photolysis. Little is known of this process, except that it is controlled by light intensity. According to the studies of McCall (1985), the photolytic half-life of triclopyr BEE in water is approximately 40 hours during the midsummer months, while that of triclopyr acid is 6 hours. The pyridinol and methoxypyridine metabolites are very unstable with a photolytic half life of only a few seconds.

According to Lee (1986), triclopyr BEE degrades in very

moist soil by hydrolysis and methylation in respective order to triclopyr, pyridinol, and methoxypyridine. This study used soil high in organic content. The soil, unless sterilised, generally contains a diverse population of micro-organisms, which could also accelerate the breakdown of triclopyr BEE. Based on this hypothesis, the breakdown of triclopyr BEE in water may have a similar pathway, (Figure 1), although not necessarily at the same rate or in the same order.

Very little information is available on the degradation of triclopyr BEE in stream sediments. The degradation process is presumably similar to that in moist soil. However, the rate is probably a function of stream water pH, temperature, organic content, microbial degradation activity, and the characteristics of the stream sediments, i.e., whether sediments are in situ materials or originate from runoff soil particles.



* Triclopyr ethyleneglycolbutylether ester

FIGURE 1. A POSSIBLE PATHWAY OF TRICLOPYR BUTOXYETHYL ESTER DEGRADATION IN WATER BASED ON LEE (1985)

3 MATERIALS AND METHODS

3.1 Study area

The study area was located at McQuire Mountain in the Chilliwack River valley, approximately 80 km east of Vancouver, B.C., (Figure 2). The study stream is situated on the east side of the spray plot at an elevation of about 200 m above and approximately 1-2 km away from the Chilliwack River. It originated as a spring within the treatment area, flows on the surface for about 50 m, then submerges underground immediately outside the plot. No fish were observed in the stream at any time.

This stream is completely covered by stream bank vegetation (alder, coppice maple, salmonberry, and birch) and was approximately 0.30 m wide and 0.05 m deep at the time of the spray operation. The estimated stream discharge was 3 - 30 L/min. It is representative of many small water courses that would most likely be missed during an on-site inspection, and subsequently oversprayed in a large scale aerial operation. To simulate an overspray situation, the buffer zone normally required for stream bank protection was not observed during the spray application. Water and sediment samples were taken at a point marked X in Figure 2.

The treatment area (approximately 21 ha) was aerially sprayed with Garlon 4TM at the rate of 0.91 kilograms active ingredient per hectare (kg a.i./ha) on September 13, 1984.

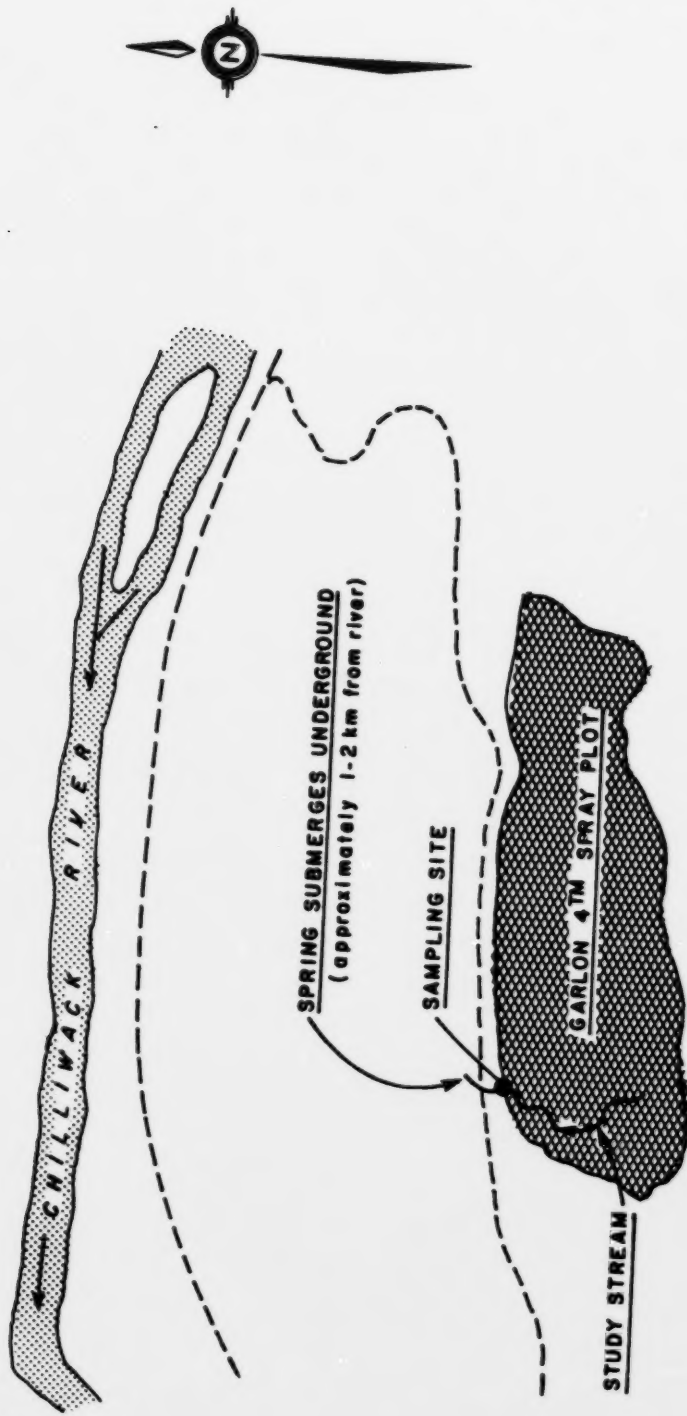


FIGURE 2 LOCATION OF GARLON 4TM STUDY AREA

3.2 Aerial Spray Application

A Bell-47 helicopter with a load capacity of 225 L of spray mix per run, was used for spray application. It was equipped with three spray jet nozzles placed equi-distance along a boom length of 2.1 m. The centre nozzle was a V-jet type (HO.25-U) complemented by two off-centre T-jet nozzles (OC-150) on either side. The V-jet nozzle had a maximum discharge capacity of 19.35 L/min, while each T-jet nozzle was capable of discharging up to 58.5 L/min. These nozzles were adjusted and set to discharge at a combined rate of 50 L/min, at an average flight speed of 50 km.p.h. The herbicide mixture was released at an average height of 9 m above the brush canopy. The flight paths were perpendicular to the study stream.

3.3 Residue Sampling Procedures

3.3.1 Water Samples: Grab water samples (10 subsamples of 40 - 50 ml at 10 to 15 seconds apart) were collected in a 450 ml amber glass at each sampling time. All bottles were rinsed with redistilled acetone and petroleum ether, and heated to 300°C for 12 hours prior to use. A piece of solvent washed and heat treated aluminium foil was used to line the opening of each bottle before capping to prevent sample contamination.

The following water sampling regime was used: Prespray; postspray, 0.10, 0.25, 0.50, 1.0, 2.0, and 4.0 h; 1, 2, 7, 11, 12, 15, 26, 28, and 59 days.

All water samples were preserved in ice soon after collection.

3.3.2 Sediment Samples: Sediment samples were collected in 500 gm wide-mouth amber glass jars. These jars were also solvent washed and heat treated before use. Ten composite sediment samples were pooled at each sampling time. The samples were collected at random along the same general section of the stream with the aid of a clean steel trowel. Sediment samples were taken from the top 3 - 6 cm of the stream bed. Solvent washed and heat treated aluminium foil was used to line the opening of each glass jar before capping. The samples were preserved ice cold in a cooler and were shipped to the laboratory within 24 hours.

The following sediment sampling regime was used: Prespray; postspray, 4.0 h; 1, 2, 7, 11, 12, 15, 26, 28, 59, 89, 125, 140, 194, 229, 271, and 319 days.

3.4 Residue Analysis

All residue analyses were conducted by the British Columbia Ministry of Environment Laboratory. Unfiltered water and sediment samples were extracted with petroleum

ether to recover the triclopyr butoxyethyl ester and 2,3,5-trichloro-methoxy pyridine. The sample was then extracted with dichloromethane under acid conditions to recover the triclopyr acid and the 3,5,6-trichloro-2-pyridinol. After methylation the extracts were cleaned up on florisil, if required, and analysed by GLC-ECD.

A quality control programme was implemented to check the recovery rates of triclopyr ester, triclopyr acid, and their metabolites. A 400-ml sample of deionized water (pH 6; temperature 20°C) was fortified with 0.100 mg/L of each chemical standard for the determination of recovery rate. Likewise, a 100-g sediment samples was fortified with 0.500 mg/kg of each chemical standard for recovery rate assessment. The average recovery rate was greater than 90 % for both water and sediment. The limit of detection for triclopyr and metabolites in water was 0.001 mg/L, and for sediment 0.02 mg/kg.

4 RESULTS.

4.1 Triclopyr residues in stream water

Triclopyr (free acid + ester) residues were detected in the stream water soon after the aerial spraying and reached a peak of 0.620 mg/L 0.50 hours after the operation commenced, (Table 1). Four hours after the spray, the concentration decreased to 0.190 mg/L. Triclopyr concentrations decreased further to 0.006 mg/L within 24 hours, and remained at the 0.001 - 0.003 mg/L level during the next two months.

The pyridinol metabolite of triclopyr was not detected in water during the first day of sampling, but appeared on the second day at a concentration of 0.07 mg/L. It remained at this low concentration for the sampling period.

4.2 Triclopyr residues in stream sediments

In the stream sediment, triclopyr was detected 4 hours after the aerial spray operation at a concentration of 0.14 mg/kg, (Table 2). Triclopyr residues decreased to 0.04 mg/kg prior to the first rainstorm, but increased to 0.12 mg/kg on the eleventh day post treatment after two rainstorms. Triclopyr concentrations were detectable during the 4 months after the spray operation. However, beyond this period, triclopyr residues were not detected above the limit

TABLE 1 PERSISTENCE OF TRICLOPYR (TOTAL ACID + BEE) AND PYRIDINOL METABOLITE IN STREAM WATER - McQUIRE MT., CHILLIWACK, B.C.

SAMPLING TIME	TOTAL TRICLOPYR ACID+BEE (mg/L)		PYRIDINOL (mg/L)		pH*	T°C
	CONTROL STREAM	TREATMENT STREAM	CONTROL STREAM	TREATMENT STREAM		
<u>PRESpray</u>	ND	ND	ND	ND	7.9	9
<u>POSTSPRAY (13/09/84)</u>						
0.10 h	-	0.290	-	ND	8.0	10
0.25	-	0.230	-	ND	-	-
0.50	-	0.620	-	ND	-	-
1.00	-	0.470	-	ND	-	-
2.00	-	0.250	-	ND	-	-
4.00	-	0.190	-	ND	7.9	-
1 day	-	0.006	-	ND	-	9
2	-	0.003	-	0.070	8.0	-
7 (rain)	-	0.003	-	0.030	-	9
11 "	-	0.003	-	0.040	-	-
12 "	-	0.002	-	0.040	7.8	-
15 (dry)	-	0.001	-	0.030	-	-
26	ND	0.002	ND	0.040	-	-
28 (rain)	-	0.003	-	0.050	-	8
59 "	ND	0.003	ND	0.060	8.2	7

ND - not detected; detection limit = 0.001 mg/L

* - pH and temperature measurements were taken for the study stream only

1 - No buffer zone was observed.

TABLE 2 PERSISTENCE OF TRICLOPYR (TOTAL ACID + BEE) AND
PYRIDINOL METABOLITE IN STREAM SEDIMENT - McQUIRE
MT., CHILLIWACK, B.C.

SAMPLING TIME	TOTAL TRICLOPYR ACID+BEE (mg/kg)		PYRIDINOL (mg/kg)		pH*	T°C
	CONTROL STREAM	TREATMENT STREAM	CONTROL STREAM	TREATMENT STREAM		
<u>PRESPRAY</u>	ND	ND	ND	ND	7.9	9
<u>POSTSPRAY (13/09/84)</u>						
4 h	-	0.14	-	0.20	7.9	10
1 day	-	0.10	-	0.07	-	-
2	-	0.05	-	0.05	-	-
7 (rain)	-	0.04	-	0.03	7.8	9
11 "	-	0.12	-	0.04	-	-
12 "	-	0.04	-	0.04	-	-
15 (dry)	-	0.04	-	0.03	-	-
26 "	-	0.08	-	0.04	8.1	-
28 (rain)	-	0.06	-	0.05	-	-
59 "	ND	0.05	ND	0.06	8.2	7
89 (snow)	-	0.02	-	0.02	-	5
125 "	-	0.02	-	0.02	-	-
140	-	ND	-	ND	-	4
194	-	ND	-	ND	-	-
229	-	ND	-	ND	8.0	7
271 (rain)	-	ND	-	ND	-	8
319	-	ND	-	ND	-	-

ND - not detected; detection limit = 0.02 mg/kg

* - pH and temperature measurements were taken for the water of the treatment stream only.

1 - No buffer zone was observed.

of detection (i.e., < 0.02 mg/kg).

The pyridinol metabolite of triclopyr was detected at 0.20 mg/kg in the stream sediment 4 hours after the aerial treatment. Decreasing concentrations of the pyridinol metabolite (i.e., 0.02 - 0.07 mg/kg) persisted for a period of 4 months. After this period, the pyridinol metabolite was not found above the limit of detection (i.e. < 0.02 mg/kg).

5 DISCUSSION

5.1 Triclopyr residues in water and sediment

In this study, triclopyr residues were detected as total triclopyr (i.e. triclopyr acid + triclopyr BEE). Water and sediment samples were not acid preserved to arrest the hydrolysis of triclopyr ester to triclopyr acid. This procedure is required to arrest hydrolysis for water with a pH greater than 7, as was the case for the study stream (pH $>7.8 < 8.2$).

5.2 Persistence of triclopyr in a forest stream

Triclopyr was detectable in stream water at very low concentrations for at least 2 months following the aerial application at 0.91 kg a.i./ha. The rapid decrease in herbicide concentrations during the first few hours post-treatment resulted mostly from dilution. However, with a slightly alkaline pH of 8.0 and a temperature of 9°C, hydrolysis and further degradation of triclopyr acid may have reduced herbicide concentrations.

Adsorption by stream sediments was another factor that reduced triclopyr concentrations in stream water. Triclopyr was detected in sediment samples shortly after the spray operation, an indication that part of the herbicide reaching the water was removed by sediment adsorption.

The low level of triclopyr detected in the stream

water during and after the first storm event one week after the spray operation suggested that negligible concentrations of triclopyr were removed from the stream bank vegetation in storm runoff water. Apparently, much of the herbicide that landed on the surface of the leaves of stream bank vegetation was either absorbed by the plants or degraded by photolysis.

There was little apparent degradation of triclopyr to its 3,5,6-trichloro-2-pyridinol metabolite in water during the first 24 hours after the spray application. On the second day post-treatment, the pyridinol metabolite was detected in water at a low concentration (0.070 mg/L). However, the pyridinol metabolite was detected almost immediately in sediments (0.20 mg/kg at 4 hours post spray). These results suggest either triclopyr was hydrolysed in the stream water and the pyridinol metabolite rapidly adsorbed onto sediments, or triclopyr residues were rapidly transformed, but only after adsorption to stream sediments.

The rate of degradation of the pyridinol metabolite in water is not well understood. According to McCall (1985), its final breakdown products are water and carbon dioxide. Whether this process occurs within a time frame of hours or days would depend on the prevailing physico-chemical conditions of the stream water.

The degradation of triclopyr and its pyridinol metabo-

metabolite in stream sediments has also not been characterized. Sediment residues may be diluted by mixing with uncontaminated soil particles. Also, triclopyr residues in sediment may be degraded by hydrolysis and photolysis (Lee, 1985).

The relative importance of these mechanisms in the turnover of triclopyr and its pyridinol metabolite in stream sediment is presently unknown. However, both chemicals persisted in decreasing concentrations to the detection limit of 0.02 mg/kg for at least 4 months in the stream sediment.

Whether sediment adsorbed triclopyr and pyridinol can be released into the aqueous environment is presently not known. The pH in the study stream was greater than 7 which may have resulted in declining sediment concentrations by the release of sediment-bound triclopyr and pyridinol metabolite into the water phase.

Attempts were made in this study to measure another metabolite of triclopyr, i.e., 2-methoxy-3,5,6-trichloropyridine in the water and sediment samples. However, this metabolite was not detected in any of the samples, which suggests it was unstable in the aquatic environment. The trichloro pyridine metabolite may be rapidly transformed to another chemical radical, possibly back to the more stable pyridinol metabolite. The recovery rate of pyridine metabolite was > 90 % for the quality control samples.

Therefore, the extraction method was adequate to recover this metabolite from the water and sediment samples. Lee (1986) studied the persistence and degradation of triclopyr in soil, but apparently no attempt was made to measure the pyridine metabolite. However, in a similar study with the triclopyr triethylamine salt (Norris et al., 1987), the pyridine metabolite was recovered in very low concentrations (0.005 - 0.061 mg/kg). It is therefore possible to recover the pyridine metabolite from soil.

REFERENCES

1. Dow Chemical of Canada Limited. "Technical Information on Triclopyr - A New Experimental Herbicide"; Technical Information Bulletin. (1981).
2. Lee, C.H.; Oloffs, P.C.; Szeto, S.Y. "Persistence, Degradation, and Movement of Triclopyr and Its Ethylene butyl ether ester in a Forest Soil"; J Agric Food Chem 34: 1075 - 1079. (1987).
3. Mayes, M.A. "Toxicity of Triclopyr Butoxyethyl Ester to Aquatic Organisms"; An affidavit for Dow Chemical Canada Inc. (1985).
4. McCall, P.J. " Environmental Fate of Triclopyr"; An affidavit for Dow Chemical Canada Inc. (1985).
5. McKinley, J.; Mason, G. " Sample Preservation for Recovery of Triclopyr Residues"; Personal communication. British Columbia Ministry of Environment Laboratory, Vancouver, B.C. (1985).
6. Norris, L.A.; Montgomery, M.L.; Warren, L. A. "Triclopyr Persistence in Western Oregon Hill

Pastures"; Bull Environ Contam Toxicol 39: (in press)

7. Szeto, S. "Sample Preservation of Water and Sediment Samples for Triclopyr Residues Recovery"; Personal communication. Agriculture Canada Research Laboratory, Vancouver, B.C. (1985).

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